COLORFAST DYES FOR WASHABLE AND DRYCLEANABLE LEATHER*

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ABSTRACT

The use of reactive dyes on glutaraldehyde-chrome combination tanned garment and glove leathers is discussed. Experimental work shows that the excellent colorfast properties of these leather dyes are added readily to the washable and perspiration-resistant qualities of this combination tannage. Data are presented on the colorfast properties of the dyed leathers. The samples were subjected to the ASTM-ALCA test for washable leather and to drycleaning tests in commercial equipment with three drycleaning agents.

INTRODUCTION

Earlier work at our laboratory demonstrated that glutaraldehyde, when used in the tanning of leather, either alone or as a retannage of chrome-tanned stock, imparted perspiration resistance to the leather (1–3). Of equal importance, from the standpoint of washable leather, was the finding that glutaraldehyde-tanned leather was quite resistant to deterioration caused by washing in warm or hot soapy water (1–3). Stability of the tannage, however, is only one of the important factors in the development of a washable leather. Other materials incorporated into the leather in post-tanning process, *i.e.,* lubricants, dyes, finishes, etc., must also resist deterioration or removal in laundering solutions. The lack of dyes resistant to soapy water and drycleaning solvents would be a major obstacle to the production of washable or drycleanable leathers in a series of appealing colors. This paper reports on the satisfactory results with one series of reactive dyes on chrome-glutaraldehyde tanned leather. These dyes are fast because they become part of the molecular structure of the leather.

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EXPERIMENTAL

A series of ICI Procion‡ M dyes were used to dye the following types of leather:

chrome-tanned cabretta

chrome-glutaraldehyde combination tanned cabretta

chrome-glutaraldehyde combination tanned garment suede.

The procedure used is outlined below. It is quite similar to the basic one listed by the supplier (4).

(*a*) The tanned skins were drummed, at room temperature, in the following ammonium hydroxide solution, for about ½ to one hour:

ammonium hydroxide (28–29 percent) : 1.5 percent of the wrung weight of skins

water : 100 percent float.

The skins were washed thoroughly in running water at least ½ hour and drained.

(*b*) The skins were next drummed for ten minutes at 50°C. in the following solution:

water : 300 percent of the wrung weight of skins

salt (NaCl) : 34 percent of the wrung weight of skins

ICI Lissatan PRN‡ : one percent of the estimated dry weight of skins.

(*c*) Added: Procion M dye : five percent of the known or calculated weight of dry skins. The dye was added to the float as a paste. Ran drum ½ hour.

(*d*) Added: sodium carbonate : 12 percent of weight of the dye plus Lissatan. Ran drum 1.5 hours. This time interval allows for good color penetration.

A routine check after 30 minutes indicated the pH at 8 and the temperature at 52°C. The pH at the end of the treatment was 8 also.

(*e*) The skins were washed in running water until free of excess or hydrolyzed dye.

(*f*) The skins were washed in warm (22–25°C.) soapy water (0.2–0.5 percent soap solution) for about five to ten minutes and then rinsed thoroughly in running water or with batch rinses until wash water was colorless.

(*g*) The skins were drummed for about ½ hour in the following formic acid solution at room temperature:

formic acid (90 percent grade) : three percent based on wrung weight of skins

water : 100 percent float at room temperature.

The pH of the liquor squeezed from the skins dropped to 3.4.

‡Trademark ICI America. The mention of specific brand names or companies is not to be construed as an endorsement over those of a similar nature not mentioned.

(*h*) The skins were washed well in running water. The skins were now ready for fatliquor and further processing.

The specimens for both the washing test and drycleaning test were cut from skins treated with dyes listed in Table I.

TABLE I

COLOR CHANGE DUE TO WASHING OF LEATHER

Procion M Dye (5%, Based on Dry Wt. of Skin)		Gray Scale Ratings*	
		C**	C-G**
Brilliant Orange	M2RS	4–5	5
Brilliant Red	M2BS	5	5
Red Brown	M4RS	5	5
Yellow	MGRS	5	5
Green	M2BS	4–5	4–5
Blue	M3GS	4–5	4–5
Mixture (%, as above)			
Gray MGS, 4% Rubine MB80, 1% Yellow MGRS, 1%	Gray	4–5	4
Gray MGS, 4.86% Rubine MB80, 0.06% Yellow MGRS, 0.024%	Blue-gray	4–5	4–5

**Key: C = Chrome-tanned leather; C-G = Chrome-tanned, glutaraldehyde-re-tanned leather.

*These ratings are for each of three wash cycles. For wash test see Reference (5). Gray scale ratings: Test Method B-57 (using International Geometric Gray Scales), American Association of Textile Chemists and Colorists (AATCC) Test Methods. 1966 Technical Manual. Research Triangle Park, P. O. Box 886, Durham, North Carolina 27702.

Wash Tests

The wash tests were done according to the ASTM-ALCA (5) procedure, wherein the specimens are washed under specified conditions in 0.5 percent soap solution for 0.5 hour at 50°C. (122°F.). Each test series consisted of four leather pieces, one unwashed, another piece washed once, a third piece washed twice, and the fourth piece washed three times. All the specimen pieces were air-dried overnight between washes. A fresh multifiber test cloth (6) was included in each wash cycle to detect any staining. Each test fiber is present as a ¼ to ⅜ inch strip in the test cloth made up of wool, viscose rayon, spun silk, nylon, bleached cotton, and acetate with a warp yarn of Dacron.

Drycleaning Tests

After some preliminary laboratory tests, full skins or large pieces of leather (garment suede) were sent out to be drycleaned in commercial equipment under

controlled conditions. One series of samples of each color was cleaned once. Another set was cleaned twice. The DuPont Division concerned with Drycleaning Products cleaned the samples with "Valclene," and the National Institute of Drycleaning cleaned samples with Stoddard Solvent or perchloroethylene, as follows:

(1) *"Valclene" (1,1,2-trichloro-1,2,2-trifluoroethane)* was used with 0.1 percent detergent in a Vic "coin-op" machine. The leather was tumbled for 3.5 minutes in solvent and detergent, drained, and rinsed in clear solvent with no detergent for two minutes. The leather was then centrifuged for 2.5 minutes and then dried with room temperature air. The entire drycleaning process was done at room temperature.

(2) *Stoddard Solvent,* containing four percent detergent, was used to clean several sets of full skins and large pieces of dyed leather. The leather was then centrifuged, rinsed in distilled solvent for five minutes, and centrifuged again. The samples were tumble-dried for 30 minutes at approximately 145°F. (62.5°C.).

(3) Perchloroethylene drycleaning was done at the National Institute of Drycleaning, although they normally do not use this solvent on leather. The samples were agitated for eight minutes in perchloroethylene containing one percent detergent and then centrifuged. The leather was then tumble-dried for 20 minutes at about 150°F. (65.5°C.).

The detergents used are widely accepted commercial products in the drycleaning industry. In the cases where the leather samples were considered too small for the equipment, the leather was fastened to large towels to make up a standard load.

TABLE II

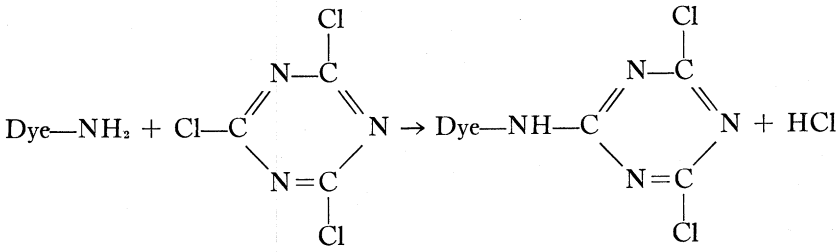
REACTIVE DYES

Commercial Name*	Manufacturer*	Type
Remazol	Carbic Hoechst	vinyl sulfone
Drimarene	Sandoz	trichloropyrimidine
Reactone	Geigy	trichloropyrimidine
Procion M	ICI	dichloro-1,3,5-triazine
Procion H	ICI	monochloro-1,3,5-triazine
Levafix	Bayer	vinyl sulfonamide
Cibacron	Ciba	monochloro-1,3,5-triazine
Primazin	BASF	acrylamide
Calcobond	Cyanamid	methylolated nitrogen

*The mention of specific brand names or companies is not to be construed as an endorsement over those of a similar nature not mentioned.

DISCUSSION AND RESULTS

An examination of the literature has shown that promising fast colors were obtained with reactive dyes. Most were developed for the textile industry and are especially useful for cottons (Table II). One type, the dichloro derivatives of cyanuric chloride (2,4,6-trichloro-*s*-triazine) (4,7–12) appeared to be most effective on leather. These are available here from ICI America, Inc.,‡ under the trade name "Procion M."

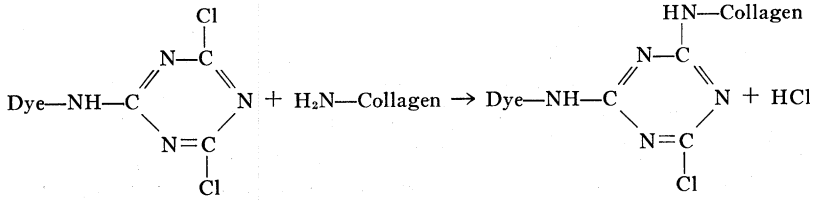


(Cyanuric Chloride) (Procion M Dye)

The published reports describing the successful use of Procion M dyes on leather have been concerned with chrome-tanned stock. The work reported here indicates that combination chrome-glutaraldehyde-tanned leather is dyed equally well. This is true even though many of the free amino groups are substituted in the glutaraldehyde tannage reaction (13, 14). Apparently, there are enough amino groups present to make the dye reaction effective. The satisfactory dye application will be obvious from the information which follows shortly on how these dyed leathers withstand our washing and drycleaning tests.

Two papers written by T. C. Mullen in 1962 and 1964 review and describe the chemistry and reactivity of these dyes, how these dyes can be used on leather, and how they differ from and compare with dyes normally used on leather (7, 8).

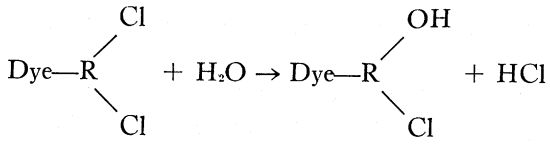
Essentially the Procion M dyestuff combines with the leather fiber with a covalent linkage. The entire dyeing process proceeds under mild temperature conditions especially suitable for leather. The reaction is shown by the following equation:



(Procion M Dye) (Leather) (Dyed Leather)

The conditions required to break the dye-collagen bond are such that the polypeptide chain of the collagen would be broken also. Leather dyes bound in such a manner are bound irreversibly.

The Procion dyes also react slowly with water, and a certain amount of hydrolysis product is formed during the course of the leather dyeing (7, 11).



This loss is minor, considering the over-all process, but all the hydrolyzed dye, as well as any unused dye, must be completely removed from the leather by thorough washing.

Fairly explicit directions (4) are available from the manufacturer which make it relatively easy to use these dyes, especially for the self-colors. Special procedures (4, 12) have been developed to produce more penetration, heavier shades, or more level shades. Discussions of the details in the procedure, such as the need for proper pH and salt concentration, etc., have been published (4, 7, 8, 10). Also, these publications give much additional technical information for those interested in technology on the practical application of dye to leather.

The various Procion M dyes have been classed into four groups according to differences in rates of penetration and shade build-up. When using mixtures of dyes to achieve certain colors, dyes classed in the same group should be used to avoid complications or poor results. Many pastels can be made readily. At this time, however, it may be difficult to produce some specially desired colors with the dyes available. The serious lack of browns for use on leather has been pointed out (9), but this color should be available soon.

Wash Tests

The resistant properties of the washable leather mentioned in the introduction should be kept in mind when reading the literature on this subject. Until recently there has been very little reference to the leather itself, and most discussions and experimental techniques on washable leather were concerned with color fading and staining. It has been found that chrome-tanned stock can become stiff and "boney" and lose its leatherlike character after several washes. For example, in the ASTM-ALCA Wash Test (5), a chrome-tanned cabretta glove leather dropped 32° in shrink temperature (87°C. → 55°C.), whereas the chrome-glutaraldehyde combination tanned leather dropped only 11°C. (88°C. → 77°C.) (3). In practice, the latter can be washed many, many times, as shown by tests using washable golf gloves (15). During the practical test involving the golf gloves, the washing procedure was quite gentle compared to the ASTM-ALCA Wash Test procedure mentioned previously (Experimental Section). The golfers were asked merely to wash the glove while wearing it, just as if they were washing their hands with soap and water at a comfortable temperature. Since the glutar-

aldehyde-treated leather has been established as resistant to the effects of washing with soap and water, the need for colorfast leather dyes that will hold up as well as the leather is quite apparent.

Although a wide variety of washfast dyes were available for textiles in the past, relatively few of the dyes were found to be fast when applied to leather. Through a process of search and selection, a number of dyes have been identified as satisfactory, especially if the leathers are not treated harshly. There are still many complaints about color running and staining, etc., but, in general, the consumer has come to realize that certain deficiencies and variable limits exist in dyed leather as compared to textiles. However, with the development of truly washable leathers these deficiencies and limits will no longer be acceptable. The Procion M dyes largely overcome these deficiencies for the colors available.

With our experimental skins, the basic color of the two tanned cabretta leathers was not the same — the glutaraldehyde-retanned skins were not as "blue" as those chrome-tanned only, because of the light amber color component imparted by the glutaraldehyde. For each dye test, skins from both tannages were dyed in the same bath. The dyed leathers from the two tannages were the same color only in several cases. There was a noticeable difference, however, in the other sets, due to the color difference of the undyed leather mentioned above. In practically all the dye tests, the chrome-glutaraldehyde skins had a more level color over the entire skin surface when compared to the straight chrome-tanned skins. The dye-leveling effect of glutaraldehyde tannage or retannage has been noticed also in the past with the more "conventional" leather dyes.

There was essentially no staining of any of the test cloth components in the wash tests described above for the dyes listed. The Gray Scale ratings, for the wash cycles listed in Table I, show very little, if any, fading or loss of the leather color after successive washes. This is true for the cabretta leather from both tannages and for the chrome-glutaraldehyde garment suede. A second golf glove test, similar to the one mentioned previously, was run using gloves made from leather dyed with these dyes (seven colors). Again, in the practical test, the leather held up very well, and the colors were fast through numerous washings.

Drycleaning Tests

Most of the trade literature concerned with the drycleaning of leather indicates the need for improved resistance to the effects of solvent on fatliquor, color, and finish (16–22). In fact, the high cost of drycleaning leather garments is due in part to the time and skill required to replace the leather lubricant and to apply a level color to the outer surface (18, 20–22). The workers in England have found the reactive dyes on leather to be fast to drycleaning (4, 8, 11, 12), as well as to washing. Technical information (4) from ICI provides a table which indicates that 19 out of 21 dyes are rated 4, 4–5, or 5 (Gray Scale Evaluation, see footnote to Table I) for fastness to Organic Solvents (perchloroeth-

ylene) according to the official SLTC Method (23). The ratings are equally good for not staining wool or cotton.

The preferred drycleaning agent for leather (especially garment suede) is Stoddard Solvent (petroleum solvent), mainly because of its milder effect on the normal leather dyes compared to perchloroethylene. The results of our drycleaning tests indicate the dyed leather colors withstood the treatments with Stoddard Solvent, "Valclene" (1,1,2-trichloro-1,2,2-trifluoroethane), and perchloroethylene. The co-operating laboratories reported that essentially no dye dissolved to discolor the cleaning solvents, and that there were no problems during the cleaning operation. The 4–5 and 5 ratings on the cleaned leathers indicated excellent retention of color. On some samples dyed with Procion Orange M2RS, Procion Blue M3GS, and Procion Red M2BS and cleaned with Valclene, the color changed from 5 to 4 after one cleaning cycle. This small additional change from that listed above may have been due to some removal, or variation in amount, of fiber lubricating or finishing agent, and not due to removal of dye.

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